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Carbonyl emission and toxicity profile of diesel blends with an animal-fat biodiesel and a tire pyrolysis liquid fuel

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HIGHLIGHTS

- An animal-fat biodiesel and two diesel blends with the animal-fat biodiesel and with a tire pyrolysis liquid (TPL) fuel have been tested in 2.0 L diesel automotive engine.
- Increase in carbonyl emissions with the biodiesel fraction in the fuel.
- Addition of TPL to diesel also increased carbonyl emissions.
- Despite specific emissions were slightly higher for 5TPL than those for DC, their reactivity is lower.
- An animal-fat biodiesel and two diesel blends with this biofuel and with a tire pyrolysis liquid fuel have been tested in a diesel engine.

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ABSTRACT

In this paper, two diesel fuels, an animal-fat biodiesel and two diesel blends with the animal-fat biodiesel (50 vol.%) and with a tire pyrolysis liquid (TPL) fuel (5 vol.%) have been tested in a 4-cylinder, 4-stroke, turbocharged, intercooled, 2.0 L Nissan diesel automotive engine (model M1D) with common-rail injection system and diesel oxidation catalyst (DOC). Carbonyl emissions have been analyzed both before and after DOC and specific reactivity of carbonyl profile has been calculated. Carbonyl sampling was carried out by means of a heated line, trapping the gas in 2,4-DNPH cartridges. The eluted content was then analyzed in an HPLC system, with UV–VIS detection.

Results showed, on the one hand, an increase in carbonyl emissions with the biodiesel fraction in the fuel. On the other hand, the addition of TPL to diesel also increased carbonyl emissions. These trends were occasionally different if the emissions were studied after the DOC, as it seems to be selectivity during the oxidation process. The specific reactivity was also studied, finding a decrease with the oxygen content within the fuel molecule, although the equivalent ozone emissions slightly increased with the oxygen content. Finally, the emissions toxicity was also studied, comparing them to different parameters defined by different organizations. Depending on the point of study, emissions were above or below the established limits, although acrolein exceeded them as it has the least permissive values.

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1. Introduction

Given that new European standard Euro VI for heavy-duty vehicles has come into force in January 2013 (EC, 2009) and considering that the light-duty counterpart will do so in September 2014 (EC, 2007), manufacturers' and researchers' eagerness to find new ways of reducing emissions is continuously growing. One of these ways is testing new renewable fuels in the already existent engines, either pure or blended with fossil fuels.

Because part of the tires has an important natural rubber content, they represent a valuable source of renewable energy. Likewise, waste tires represent a serious pollution problem in terms of waste disposal since about 1.5 billion tires are sold worldwide each year (ETRMA, 2011), while 4 billion are currently in landfills and stockpiles worldwide (WBCSD, 2008). Nowadays, both the EU27 plus Turkey and the US generate annually around 300 million of waste tires (ETRMA, 2011; Kwon et al., 2012) and have an increasing trend. A way of making use of tires and turning them into diesel fuel is by means of pyrolysis. This process is receiving renewed interest and attention to tackle the waste tire disposal problem while allowing energy recovery. Pyrolysis, also termed

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thermal distillation or thermolysis, is a thermochemical treatment that allows breaking apart chemical bonds by means of a thermal decomposition under non-oxidative conditions (inert atmosphere or vacuum) (Martínez et al., 2013a). The resultant products can be easily handled, stored and transported. Although the liquid fraction (tire pyrolysis liquid – TPL) is completely miscible with diesel fuel (Islam et al., 2008), it has some critical properties in comparison to diesel fuel. As showed elsewhere (Martínez et al., 2013b), density, cold filter plugging point (CFPP), water content and total acid number (TAN) as well as sulfur content, need to be addressed to meet the requirements established for diesel fuels (standard EN 590). In spite of these facts, blending TPL with diesel fuel may help to reduce these limitations and for this reason TPL represents a feasible alternative for diesel fuels as long as it is blended in low concentrations.

Nevertheless, just a limited number of studies show the usage of TPL in diesel engines in comparison to the large number of works regarding the waste tire pyrolysis process as recently reviewed (Martínez et al., 2013a). Generally speaking, these few works show different results of the effect of TPL on both diesel engine performance and emissions and this is ascribed to the different properties of TPL as well as differences in engine technologies and operational conditions. For instance, Doğan et al. (2012) did not find major effects on the engine output power and the brake thermal efficiency with respect to those of diesel fuel when a refined and desulfurized TPL was blended up to 50 vol.%. Smoke opacity, CO and THC emissions decreased as TPL increased in the blend while NO_X increased. İlkılıç and Aydın (2011) also studied the engine performance and regulated emissions of TPL/diesel blends. They found that TPL produces higher CO, THC, SO_2 and smoke emissions than conventional diesel fuel. Similarly, Hariharan et al. (2013) showed the performance, emission and combustion characteristics of a DI diesel engine fuelled with TPL and diethyl ether as ignition improver. As it can be checked, researchers in this field only focused on regulated emissions.

Contrary to liquid fuels from tires, biodiesel has been widely studied as substitutive of fossil fuels for many years. As result, non-regulated emissions such as carbonyl ones have been analyzed due to their atmospheric instability and their potential to form ozone in lower atmosphere layers (Ballesteros et al., 2012). Among the different origins that biodiesel can have, tallow biofuel, or biofuel from the transesterification of both animal fats and farming wastes, has reached some importance since those feedstock do not threaten food supply and are therefore not the source of "food or fuel" controversy (EC, 2002). However, data on carbonyl emissions are limited in literatures (Ballesteros et al., 2011; Magara-Gomez et al., 2012) and for this reason their importance for addressing the environmental and energy concerns derived from petroleum-based fuels.

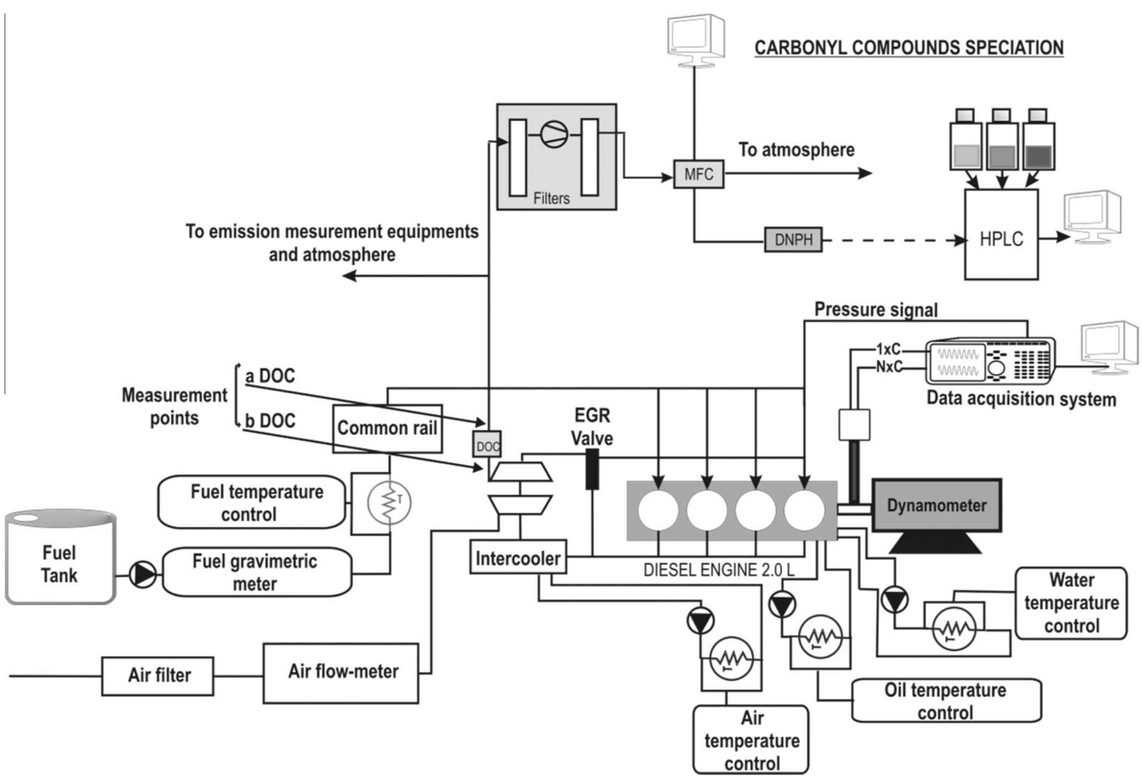

Fig. 1. Test bench diagram.

Table 1
Diesel engine specifications.

Fuel injection system	DI, common-rail	Compression ratio	16:1
Cylinders	4	Displacement (cm^3)	1994
Valves	16	Maximum power (kW)	111 @ 4000 rpm
Bore (mm)	84	Maximum torque (Nm)	323.5 @ 2000 rpm
Stroke (mm)	90	Weight (kg)	215

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